

For any position of the short mercury thread, the diameter is inversely proportional to the square root of the thread length.

$$\frac{d_1}{d_0} = \sqrt{\frac{\lambda_0}{\lambda_1}} \quad (14)$$

where d_0 is the average diameter of the capillary tube.

We may compute the percentage deviation of the diameter at any point from the average diameter from the equation

$$D = 100 \left(\sqrt{\frac{\lambda_0}{\lambda}} - 1 \right) \quad (15)$$

in which

D = the percentage departure.

λ = the observed thread length.

λ_0 = the average of the observed thread lengths.

Columns 7 and 8 of table 1 list the maximum positive and negative departures from the average diameter, and column 9 lists the average departure of the individual determinations from the average diameter.

The tubes studied were not all made by the same manufacturing process. The starting material in each case was tubing having an outside diameter of approximately 1½ in. Tubes 1 to 3 were drawn

over steel mandrels through dies that reduced the diameter by about one-quarter at each step, until the inside diameter was about 0.09 in. Thereafter the reductions were accomplished without mandrels.

A second set of tubes (not listed in table 1) were obtained from a manufacturer who drew the tubes to the finish diameter over mandrels. It was found that the rolls used in loosening the tubing from the mandrels were not perfectly centered and therefore produced a periodic variation in the diameters, which rendered the tubes unuseable. The variations amounted to as much as ± 5 percent. Attempts were made to eliminate these differences by successive drawing through external dies, with slight diameter reduction. After four stages, the variations were somewhat reduced, but the periodic character persisted and the tubes were abandoned. Tubes 8 to 12, with heavier walls, were then supplied by the same manufacturer. In a lot of six tubes, only one was found to have unsatisfactory characteristics.

V. Summary

It has been found practical to apply the method of Fisher to the determination of flow constants for metallic capillary tubing and to study the uniformity of such tubing by X-ray photography of a mercury thread within the tube. Eight pieces of tubing were selected from a group of twelve, having a maximum deviation from the average diameter of 2.5 percent. Flow constants for these eight tubes were determined.

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Mass Spectra of Some Simple Isotopic Molecules

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The mass spectra of H_2 , D_2 , T_2 , HD , and HT have been measured with a Consolidated mass spectrometer with 50-volts ionizing voltage and with a constant magnetic field. The following ratios of atom ions to molecule ions were observed: $H^+/H_2^+ = 0.0201$, $D^+/D_2^+ = 0.0096$, $T^+/T_2^+ = 0.0061$, $H^+/HD^+ = 0.0096$, $D^+/HD^+ = 0.0097$, $H^+/HT^+ = 0.0085$, and $T^+/HT^+ = 0.0068$. The ratios for T_2 and HT were derived from spectra of two samples containing 91 and 37 atomic percent of T in equilibrium with H . Theoretical values for the ratios were computed for ionization involving transition into the Σ_g state of the molecule ion. These values are lower than the observed ratios, because transitions to higher repulsive states contribute to the observed values at 50-volts ionizing voltage.

Mass spectra of CO and CO_2 containing about 54 atom percent C^{13} were measured under standard operating conditions. For CO the ratio $C^{12+}/C^{13}O^+ = 0.0540$ and $C^{13+}/C^{13}O^+ = 0.0514$. For CO_2 , the ratios are $C^{12}O^+/C^{13}O_2^+ = 0.0868$, $C^{13}O^+/C^{13}O_2^+ = 0.0824$, $C^{12+}/C^{12}O^+ = 0.0564$, and $C^{13+}/C^{13}O^+ = 0.0542$.

A theory of the isotope effect in CO involving simplifying assumptions indicates that the relative probability of producing C^{12+} is 3.5 percent greater than the probability of producing C^{13+} , as compared with an observed difference of 5 percent.

I. Isotopic Hydrogen Molecules

1. Introduction

Mass spectra of H_2 and D_2 have been investigated frequently [1],¹ and a recent paper by Friedel and

Sharkey [2] gives the spectrum of HD . The present research was undertaken because of the opportunity to obtain some very pure HD and a sample of tritium of relatively good purity. Hydrogenic spectra are of interest because it is possible to compute theoretically from the Franck-Condon principle the relative probabilities of producing atom ions from the differ-

¹ Figures in brackets indicate the literature references at the end of this paper.

ent isotopic molecules, and a comparison of theory and experiment gives information on the mechanism of dissociation. Stevenson [3] has carried out the theoretical computations for H_2 and D_2 . Data on these molecules are also of practical importance in the analysis of isotopic mixtures.

2. Experimental Procedure

A 180° Consolidated mass spectrometer was used, operated with a constant magnetic field requiring 3,800 v to focus mass 1 and using an ionizing voltage of 50 v. Pumps were speeded up, and pressure in the ionization chamber was kept fairly low to maintain a high vacuum in the spectrometer. This is a necessary precaution [4] with hydrogen, but as a result the atom ion peaks are rather small for accurate measurement. There are no triatomic ions under these conditions.

Very pure D_2 and HD were prepared by fractionation at liquid hydrogen temperatures by Fookson, et al. [5] of this Bureau. HD was fractionated from crude HD prepared by the reaction of D_2O and lithium aluminum hydride [6]. The tritium was obtained from Argonne National Laboratory and was 91 percent of T and 9 percent of H. It was separated from He^3 16 days before the spectrum was measured. A small correction amounting to 0.16 percent was applied for He^3 on the basis of a half-life of 12 years for tritium and the measured sensitivity (current per unit pressure) of He^4 .

Table 1 gives the experimental results under columns headed "Expt." Data for H_2 and D_2 are consistent with published results. Friedel and Sharkey [2] report for HD values of 0.82 percent for H^+ and 1.13 percent for D^+ . The value for D^+ of HD in table 1 is an upper limit assuming H_2^+ is zero. The value of 0.97 percent is the lowest value obtained in several experiments, but H_2^+ may contribute an amount of the order of 0.1 percent to mass 2. In the tritium both T_2 and HT are present and contribute to the mass 3 peak. The separate contributions were evaluated by obtaining the spectrum of the original sample containing 9 percent of H, then adding hydrogen and equilibrating the mixture in contact with an incandescent filament to obtain a mixture of 67 percent of H and 33 percent of T and repeating the measurement. In the first spectrum T_2 was large and TH small, and in the second spectrum the reverse was true. From the two spectra, values are derived for both T^+/T_2^+ and T^+/TH^+ .

Table 1 includes the sensitivity (current per unit pressure) for the molecule ions. They are nearly equal except for T_2 , which is about 10 percent lower than the other values. This is not surprising, as the ion accelerating voltage is only a third as much for T_2 as for H_2 .

3. Theory

The ratio of atom ions to molecule ions can be computed by means of the Franck-Condon principle for the case of a transition from the normal state of hydrogen to the stable Σ_g state of the molecule ion.

TABLE 1. Mass spectra of hydrogen molecules

m/e	H_2		HD		D_2		HT		T_2	
	Expt.	Theor.	Expt.	Theor.	Expt.	Theor.	Expt.	Theor.	Expt.	Theor.
1.....	2.01	1.9	0.96	0.7	0.85	0.6
2.....	100	0.97	0.7	0.96	0.8
3.....	100	0.68	0.6	0.61	0.3
4.....	100	100
6.....	100
Sensitivity ..	20.0	21.2	19.5	17.8

* Ion current per unit pressure in gas reservoir for the molecule ions in arbitrary units.

Dissociation into an atom ion occurs if a vertical line from the normal state intersects the potential energy curve of the molecule ion at a point above the dissociation limit of the molecule ion. That is, the fraction of molecules with atoms inside a critical internuclear distance r_c will dissociate on ionization and, for H_2 , about 2 percent of the atoms fall inside r_c and give atom ions. The potential energy curves of the Franck-Condon diagram and r_c remain unchanged in isotopic molecules. However, the radial distribution of atoms in the normal state is narrower for the heavy isotopes. This materially reduces the small fraction of atoms that fall inside r_c . Stevenson [3] has published computations for H_2 and D_2 , and we have extended the computations to the other isotopic molecules. The values included in table 1 are subject to appreciable computational error, as they depend critically on the shape of the potential energy curves.

Experimental values are not exactly comparable with the theoretical values, for atom ions can also be produced by transitions to higher repulsive states of the hydrogen ion; namely, the Σ_u state and the doubly ionized state. The most probable transition to a repulsive state requires about 10 v in excess of the threshold for appearance of atom ions and results in ions of high kinetic energy. These ions are not collected efficiently by the mass spectrometer, and consequently they make only a small contribution to the atom ion peak. Hagstrum and Tate [7] have studied mass spectra of diatomic molecules and velocity distribution of the atom ions and have interpreted the results in terms of Franck-Condon diagrams. Their results for H_2 show the magnitude of the contribution of the high velocity atom ions from repulsive states.

The contribution of atom ions from repulsive states accounts for the fact that experimental results for 50-v electrons are always somewhat greater than the theoretical values. In the dissociation of HD the H^+ ion will have twice the kinetic energy of D^+ . In the mass spectrum obtained with a constant magnetic field the kinetic energy received from the electric field will also be twice as large for H^+ , so both ions should be collected with equal efficiency. Similarly H^+ and T^+ of HT should be measured with equal efficiency. The experimental observation that T^+ is less abundant than H^+ is unexplained. In other respects the experimental data seem quite consistent with theoretical predictions.

A mixture of D₂ and tritium was equilibrated in contact with an incandescent filament, but the spectrum of the mixture containing six isotopic molecules in appreciable amounts was too complicated to permit derivation of the DT spectrum. Theoretical computations indicate that D⁺ and T⁺ will each be 0.35 percent of DT⁺.

II. Mass Spectra of CO and CO₂

1. Introduction

One would expect to find isotope effects in the mass spectra of molecules other than hydrogen, but the isotope effects will be much smaller when there is a relatively small difference in the mass of the isotopes involved. There is ample evidence for such effects both in mass spectra and in thermal dissociation. Dibeler, Mohler, and Reese have reported such effects in the spectrum of nitrogen containing 65 percent of N¹⁵ [8]. Beeck, et al. [9] have reported that the dissociation probabilities of C¹²-C¹² and C¹²-C¹³ bonds of molecule ions formed from propane-1-C¹³ differ by about 20 percent, whereas Stevenson, et al. [10] find that in the thermal cracking of this molecule there is an 8-percent greater frequency of rupture of C¹²-C¹² bonds than of C¹²-C¹³ bonds. Thermal decomposition of oxalic acid to give CO, CO₂, and H₂O has been studied by Lindsay, McElcheran, and Thode [11], and on the basis of the distribution of C¹³ in CO and CO₂ they concluded that the dissociation of a C¹²-O¹⁶ bond is approximately 3.5 percent more frequent than the dissociation of a C¹³-O¹⁶ bond.

2. Experimental Procedure

We have measured the relative abundance of the ions containing C¹² and C¹³ in the mass spectrum of carbon monoxide and of carbon dioxide with high concentration of C¹³. Carbon dioxide was evolved in vacuum by the action of concentrated sulfuric acid on barium carbonate containing 54 atom percent of C¹³. A portion of the product was almost completely reduced to carbon monoxide over hot zinc according to the method of Bernstein and Taylor [12]. Traces of carbon dioxide were removed in a liquid nitrogen trap.

Mass spectra were obtained by using conventional techniques. The energy of the bombarding electrons was nominally 50 v, and the temperature of the ionization chamber was about 245° C. Data reported here were measured at constant magnetic field and varying ion accelerating voltage. In the case of CO₂, however, spectra were also obtained at constant ion accelerating voltage by varying the magnetic field. These spectra differ slightly in the ratios CO⁺/CO₂⁺ and C⁺/CO₂⁺, but the relative amounts of isotopic ions were the same within the estimated experimental error.

3. Results

Table 2 gives the mass spectra of carbon monoxide and carbon dioxide containing 54 atom percent C¹³. Corrections have been made for the contributions of

oxygen isotopes to the isotopic peaks. Columns 1 and 2 give the mass to charge ratio and the ion species for carbon monoxide. Column 3 gives the abundance of each ion relative to the most abundant ion, *m/e*=29. The ratio C¹²/C¹²O¹⁶ equals 0.0540, whereas the ratio C¹³/C¹³O¹⁶ equals 0.0514. The ratio of these two values, 1.05, is a measure of the relative probability of dissociating a C¹²-O¹⁶ bond as compared with a C¹³-O¹⁶ bond in the CO molecule.

TABLE 2. Mass spectra of CO and CO₂ containing approximately 54 atom percent of C¹³

[Correction has been made for oxygen isotopes]

Carbon monoxide			Carbon dioxide		
<i>m/e</i>	Positive ion	Relative abundance	<i>m/e</i>	Positive ion	Relative abundance
12	C ¹²	4.68	12	C ¹²	4.91
13	C ¹³	5.14	13	C ¹³	5.42
16	O ¹⁶	3.16	16	O ¹⁶	15.4
28	C ¹² O ¹⁶	86.7	28	C ¹² O ¹⁶	7.55
29	C ¹³ O ¹⁶	100.0	29	C ¹³ O ¹⁶	8.24
			44	C ¹² O ₂ ¹⁶	87.0
			45	C ¹³ O ₂ ¹⁶	100.0

Columns 4, 5, and 6 of table 2 give the mass spectrum of carbon dioxide relative to the most abundant ion, *m/e*=45. For the dissociation of a single C-O bond, the ratio C¹²O¹⁶/C¹²O₂¹⁶ equals 0.0868, whereas the ratio C¹³O¹⁶/C¹³O₂¹⁶ equals 0.0824. Again, the ratio of these two values, 1.05, is a measure of the probability of dissociating a C¹²-O¹⁶ bond, as compared with a C¹³-O¹⁶ bond. For the dissociation of two C-O bonds, the ratio C¹²/C¹²O₂¹⁶ equals 0.0564, whereas the ratio C¹³/C¹³O₂¹⁶ is 0.0542. Rather surprisingly the ratio of these values, 1.04, indicates that the dissociation of two C¹²-O¹⁶ bonds is only 4 percent more frequent than the dissociation of two C¹³-O¹⁶ bonds. Measurements made on a sample of carbon dioxide containing 4 atom percent of C¹⁴ gave similar, though less accurate, results for the relative probability of dissociating C¹²-O¹⁶ bonds and C¹⁴-O¹⁶ bonds. The results on the preferential dissociation of a C¹²-O¹⁶ bond compared with a C¹³-O¹⁶ bond in the ionization process are similar to the results of Lindsay, McElcheran, and Thode [11] on thermal dissociation of oxalic acid.

4. Discussion

Similar effects of isotopes on the dissociation probabilities of other molecules have been observed in this laboratory. From analysis of the mass spectrum of nitrogen [8] containing 65 atom percent of N¹⁵ it was found that an N¹⁴-N¹⁴ bond dissociates about 11 percent more frequently than an N¹⁵-N¹⁵ bond. The relative probability of dissociating an N¹⁴-N¹⁵ bond was less accurately determined, but the value is intermediate between the values for N₂¹⁴ and N₂¹⁵.

It is to be expected that isotope effects in CO and N₂ can be explained in terms of the Franck-Condon

principle, except for the difficulty that potential energy curves for the molecule ion states are not accurately known. D. P. Stevenson in an unpublished paper presented before the New Orleans meeting of mass spectrometer users in May 1950 pointed out that the isotope effect in N_2 can be estimated without detailed knowledge of the upper potential energy curve. The observation that N^+ is about 6.7 percent of N_2^{4+} indicates that in the radial distribution of atoms in the normal state, 6.7 percent of the atoms fall inside the critical internuclear distance for dissociation in the ionized state. From the known distribution of atoms in the normal state, the critical internuclear distance can be computed. In N_2^+ the distribution of atoms will be reduced by an amount that will result in a 7-percent reduction of the fraction inside the critical internuclear distance. This is considered in substantial agreement with the observed difference of 11 percent.

This interpretation is supported by the research of Hagstrum and Tate [7] on the velocity distribution of atom ions as related to the Franck-Condon diagrams. The velocity distribution of N^+ ions indicates that dissociation comes primarily from a process of the type postulated by Stevenson. This is also true of C^+ from CO. On the basis that 5.4 percent of C atoms of $C^{12}O^{16}$ fall inside the critical internuclear distance, it is estimated that in $C^{13}O^{16}$ there will be a 3.5-percent reduction in the fraction inside the critical distance. The observed difference was 5 percent. Exact agreement is not expected, for the theory assumes that a single transition process gives rise to C^+ . It is known that at least two transitions give C^+ ; one or more giving C^+ and O and one or more giving C^+ and O^- .

III. Conclusion

Isotope effects in the diatomic molecules, hydrogen, nitrogen, and C^+ of CO seem to be accounted for by the Franck-Condon principle and the fact that the radial distribution of atoms in the normal state depends on the mass of the isotopes. In these molecules a small fraction of the atoms in the normal state falls inside the critical internuclear distance for dissociation in the ionized state, and this condition leads to a relatively large isotope effect. The research of

Hagstrum and Tate [6] on the ionization of diatomic molecules indicates that production of O^+ from O_2 and of N^+ from NO will be similar in this respect to N_2 . However, for the transitions giving O^+ from CO and O^+ from NO, roughly half and three quarters respectively of the atoms fall inside the critical radius and the isotope effect would presumably be much less. One would not expect the relative amount of O^{14+} from the isotopic mixture of $C^{12}O^{16}$ and $C^{13}O^{16}$ of table 2 to be significantly different from normal CO, and this is experimentally observed.

Although similar effects may be expected in polyatomic molecules, it is not feasible to predict quantitatively the isotope effects in CO_2 or more complicated molecules. It may be coincidental that production of C^+ and CO^+ from CO_2 show almost the same isotope effect as C^+ from CO. The theory of diatomic molecules indicates that each dissociation process will have a characteristic isotope effect, and values of zero or even negative values are not excluded.²

IV. References

- [1] N. Bauer and J. Y. Beach, *J. Chem. Phys.* **15**, 150 (1947).
- [2] R. A. Friedel and A. G. Sharkey, Jr., *J. Chem. Phys.* **17**, 584 (1947).
- [3] D. P. Stevenson, *J. Chem. Phys.* **15**, 409 (1947).
- [4] R. E. Honig, *J. Chem. Phys.* **16**, 837 (1948).
- [5] A. Fookson, P. Pomerantz, and E. H. Rich, *Science*, in press.
- [6] I. Wender, R. A. Friedel, and M. Orchin, *J. Am. Chem. Soc.*, **71**, 140 (1949).
- [7] H. D. Hagstrum and J. T. Tate, *Phys. Rev.* **59**, 354 (1941).
- [8] V. H. Dibeler, F. L. Mohler, and R. M. Reese, *J. Chem. Phys.* **18**, 156 (1950).
- [9] O. Beeck, J. W. Otvos, D. P. Stevenson, and C. D. Wagner, *J. Chem. Phys.* **16**, 255 (1948).
- [10] D. P. Stevenson, C. D. Wagner, O. Beeck, and J. W. Otvos, *J. Chem. Phys.* **16**, 993 (1948).
- [11] J. G. Lindsay, D. E. McElcheran, and H. G. Thode, *J. Chem. Phys.* **17**, 589 (1949).
- [12] R. B. Bernstein and T. I. Taylor, *Science* **106**, 498 (1949).
- [13] O. Schaeffer and J. Hastings, *Quarterly Progress Report*, p. 31 (Brookhaven National Laboratory, Mar. 31, 1950).

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² A progress report by O. Schaeffer and J. Hastings of the Brookhaven National Laboratory [13] on mass spectra of H_2 , D_2 , and T_2 has appeared since this paper was written. They report ratios of atom ions to molecule ions obtained from ionization by electrons of 30 electron volts, and values are considerably smaller than values reported in table 1 at 50 ev, as is to be expected. In other respects their results are comparable with ours.